ON THE RAMAN SPECTRA OF ETHYLENE DICHLORIDE IN SOLUTIONS OF DIFFERENT STRENGTHS*

By SUKHENDU BIKASH BANERJEE
Optics Department, Indian Association for the Cultivation of Science, Calcutta—32

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Plates VI A, B

ABSTRACT—The Raman spectra of solutions of ethylene dichloride of concentrations 25% and 50% by volume in heptane and cyclohexane have been studied and the relative intensities of the lines 754 cm^{-1} and 654 cm^{-1} have been measured in each case and compared with the values observed in the case of pure liquid. It has been observed that the ratio I_{754}/I_{654} increases when the liquid is dissolved in either of the two solvents to make 50% solutions and the ratio increases further when the concentration is diminished. It is pointed out that these results support the conclusion arrived at by Bishui (1948) that one of these two lines is due to associated molecules and are contradictory to the conclusions drawn by Kuratani (1952) that association of molecules has nothing to do with origin of these lines

INTRODUCTION

It was first pointed out by Sirkar and Bishui (1945) that in the liquid state some of the molecules of ethylene dibromide might exist as associated pairs. Bishui and Sanyal (1947) studied the relative intensities of the lines 660 and 551 cm^{-1} in the Raman spectra of ethylene dibromide dissolved in various solvents and came to the conclusion that the line 551 cm^{-1} is due to associated group of molecules while the line 660 cm^{-1} is due to single molecules. Bishui (1948) also studied the Raman spectra of ethylene dichloride (1,2 dichloroethane) and 1,1-dichloroethane in the liquid and solid states and came to the conclusion that the line 654 cm^{-1} of the former liquid is due to associated molecules while the line 754 cm^{-1} is due to single molecules. Recently, Kuratani (1952) has studied the infra-red absorption bands of ethylene dichloride (1,2-dichloroethane) in solution in various solvents and has studied the intensity-ratio of the bands 1284 and 1230 cm^{-1} assumed to be due to gauche and trans forms respectively. He has observed that the intensity-ratio of the two absorption bands does not change with the change of concentration of solution of ethylene dichloride in carbon tetrachloride and carbon disulphide, and assuming the two bands to be due respectively to the gauche and trans forms of the molecule, he has concluded that the association theory put forward by Bishui (1948) is contradicted by these results.

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On going through the results reported by Bishui and Sanyal (1947), however, it is found that the relative intensities of the lines 660 and 551 cm^{-1} of ethylene dibromide do not change appreciably when the liquid is dissolved in carbon tetrachloride, and therefore, it cannot be expected that the intensity ratio will change with change in the concentration of the solution. On the other hand, Bishui and Sanyal (1947) observed that the intensity-ratio changes considerably when the liquid is dissolved in hexane and such a change might be expected also in the case of solution of ethylene dichloride in hexane or similar solvents, and the influence of concentration on the intensity-ratio could be expected only in the case of these solutions in which the intensity of the line 654 cm^{-1} of ethylene dichloride is less than that for the pure liquid. It was, therefore, thought worthwhile to study the influence of concentration on the relative intensities of the lines 754 and 654 cm^{-1} of ethylene dichloride dissolved in suitable solvents in different proportions. The results for solutions of ethylene dichloride in heptane and cyclohexane have been dicussed in prssent paper.

EXPERIMENTAL

The liquid ethylene dichloride and the two solvents, cyclo-hexane and the heptane used in the present investigation were of chemically pure quality and were supplied by B. D. H. and May Baker. The liquids were distilled in vacuum in large quantities before use. The Raman spectrum of the pure liquid was first photographed, using a Fuess glass spectrograph giving a dispersion of about 12 A.U. per mm in the 4046 Å region and Ilford Zenith plates. Two solutions of known strengths were prepared first with heptane as the solvent, the strengths being about 65% and 38% by weight. The Raman spectra of these two solutions were recorded using plates from the same packet and developing them exactly in the same way as the plate for the pure liquid mentioned above. The process was repeated for the solutions of the liquid in cyclohexane of strengths 62% and 35% by weight. The Wood's tube containing either the pure liquid or the solutions was provided with a jacket filled with a dilute solution of sodium nitrite which cut off the 3650Å group of mercury lines and prevented production of continuous fluorescence by the solution or the pure liquid. The strength of this filtering solution was the same in all the cases. Intensity marks were next taken on another Zenith plate taken from the same packet by varying the width of the slit of the spectrograph and using a glowing tungsten filament bulb as the source of continuous radiation. Microphotometric records were taken with a Kipp and Zonen type self-recording microphotometer. Blackening-log intensity curves were drawn for the wavelengths corresponding to the lines 654 cm^{-1} and 754 cm^{-1} excited by both the 4077 Å and 4358 Å lines of mercury. The values of I_{754}/I_{654}, the ratio of intensities of the lines 754 and 654 cm^{-1} were then calculated for the pure liquid and for the solulions using these blackening-log intensity curves.

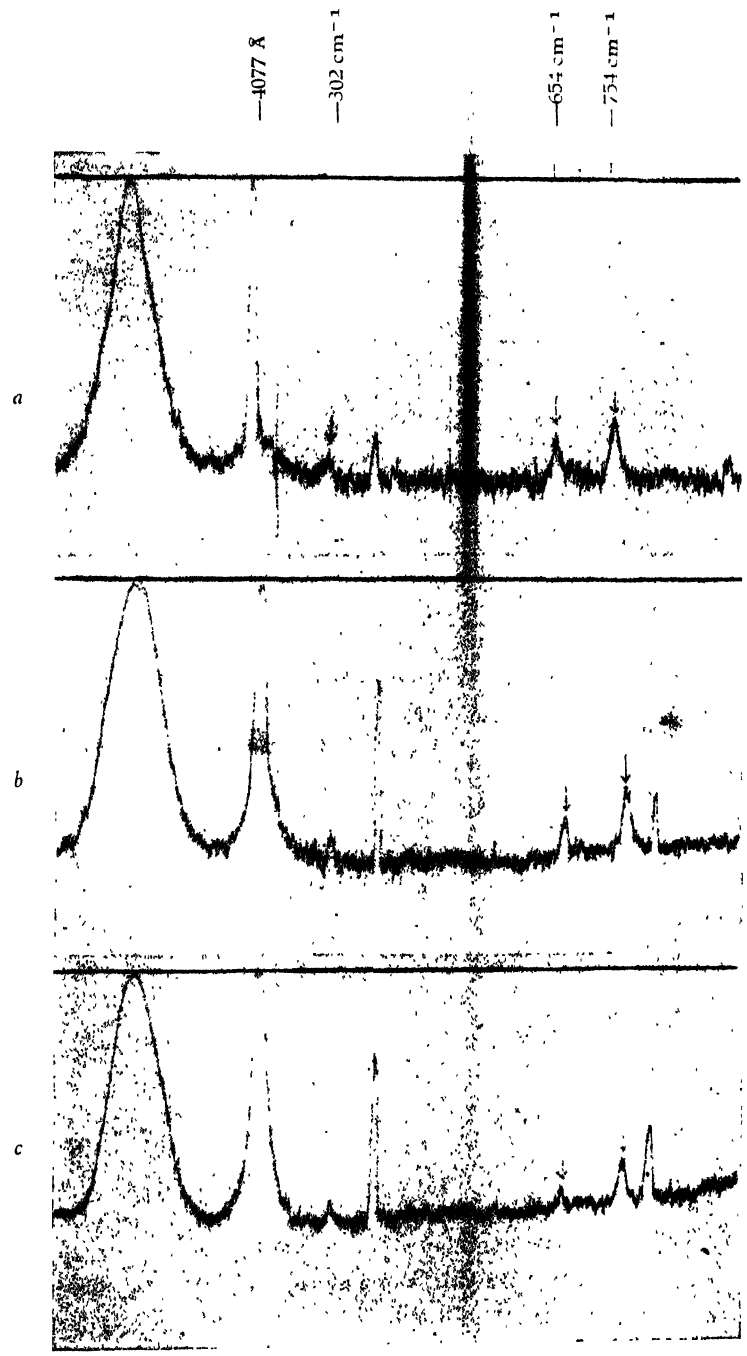

Fig. 1

Microphotometric records of Raman spectra.

(*a*). Ethylene dichloride, liquid at 28°C

(*b*). 50% Solution (by volume) of ethylene dichloride in cyclohexane

(*c*). 25% " " " " " " " "

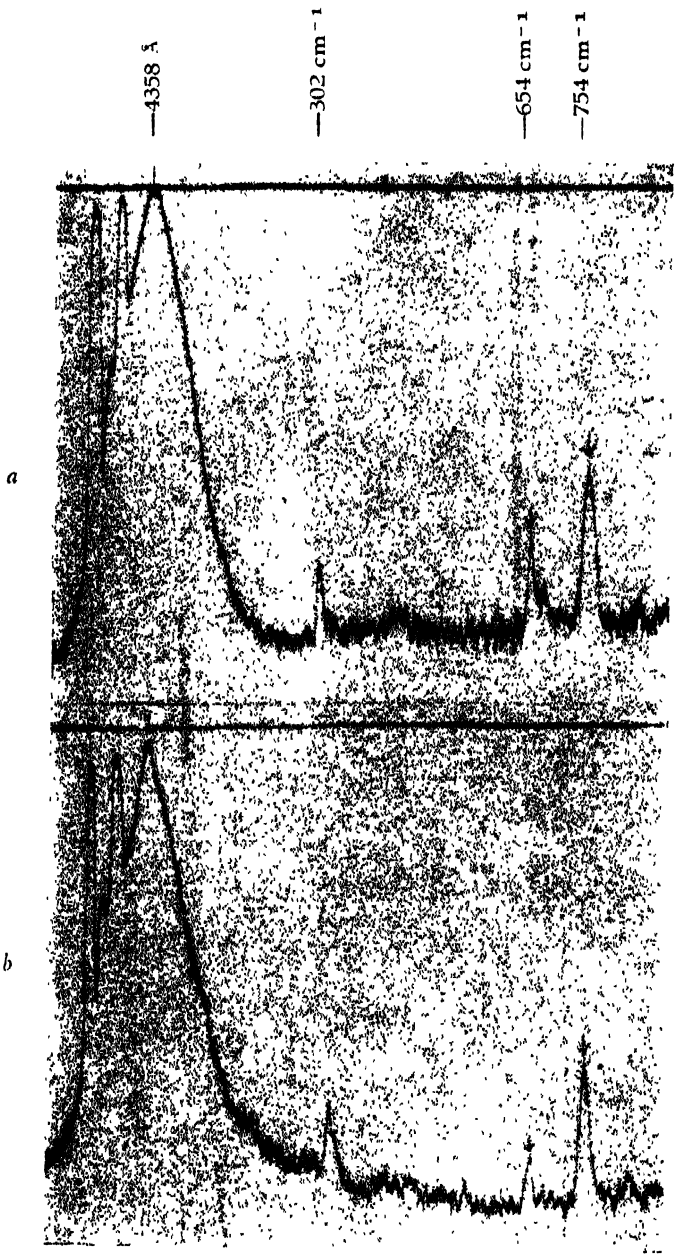

Fig. 2

Microphotometric records of Raman spectra

(*a*) 50% solution (by volume) of ethylene dichloride in heptane

(*b*) 25% " " " " " " " "

RESULTS AND DISCUSSION

The microphotometric records of the spectrograms for the pure liquid and solutions in cyclohexane are reproduced in Plate VIA and those for the solution in heptane are reproduced in Plate VIB. The values of $I_{751} : I_{654}$ calculated with the help of these records and the blackening-log intensity curves are given in Table I. In calculating these values the relative widths of the two lines were taken into account, and therefore, the values given in Table I are those of integrated intensities. The temperature was about 28°C in all the cases.

TABLE I

Solvent used	Concentration of $C_2H_4Cl_2$ by weight	I_{751} / I_{654}
Heptane	100%	2.0
	65%	3.1
	38%	4.3
Cyclohexane	100%	2.0
	62%	2.8
	35%	3.1

It can be seen from Table I that the ratio of the integrated intensities of the lines 754 and 651 cm^{-1} for the pure liquid at 28°C is 2.0 which is the same as the value reported by Mazumder (1953) for the liquid at 135°C. This ratio therefore does not change appreciably with the rise of temperature. The value of the ratio, however, increases considerably as the liquid is dissolved either in cyclohexane or in heptane even for a concentration just above 60%. This change is larger in the case of solution in heptane than for the solution in cyclohexane. The ratio increases in the case of solution in heptane from 3.1 to 4.3 when the concentration is diminished from 65% to 38%. In the case of the solution in cyclohexane also the ratio increases with dilution of the solution, but this increase is smaller than that in the former case. These results can be clearly seen from a comparison of the relative intensities of the lines 302 cm^{-1} and 654 cm^{-1} in the spectograms due to the pure liquid and the solution in cyclohexane reproduced in Plate VIA.

The results thus demonstrate the dependence of the intensity-ratio on the concentration of the solution. Such an influence can be expected if the line 654 cm^{-1} is assumed to be due to associated molecules and the line 754 cm^{-1} is attributed to the single molecule. The hypothesis that the liquid consists of molecules of two forms the relative populations, of which are determined by the temperature cannot explain these results. Hence the conclusion arrived at by Kuratani (1952) is not supported by the results of the present investigations. On the other hand, these results support the

view expressed by Bishui and Sanyal (1947) that association of some of the molecules in the liquid state to form pairs gives rise to the line 654 cm^{-1}. The formation of virtual bond between neighbouring molecules may either alter the orientation of one half of the molecule about the other half or it may alter the strength of the C-Cl bond. The results reported by Mazumder (1953) also show that there is a catastrophic change in the relative intensities of the lines 654 and 754 cm^{-1} with the vaporization of the liquid without change of temperature. Those results also support the view that some strong intermolecular field is responsible for producing the change in relative intensities of the two lines mentioned above.

The fact that different solvents have different types of influence on the relative intensities of the two lines shows that the relative numbers of the molecules of two forms which are assumed to be present in the liquid by previous workers (Mizushima and Morino, 1938) depend on intermolecular field. As it is observed in the present investigation that saturated hydrocarbon molecules as solvents have greatest influence on the relative numbers of the two forms it is quite probable that the number changes in this case owing to breaking up of the associated molecules in the solution.

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